3-AMINOPHTHALIMIDE AND

AZO DYE OF A CONTAINING CARBAMOYL MOIETIES Guenther Ruider, Frankenthal, and Peter Dimroth, Ludwigshafen, Germany, assignors to Badische Anilin- & Soda-Fabrik Aktiengesellschaft, Ludwigshafen (Rhine), Germany

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ABSTRACT OF THE DISCLOSURE

This invention is directed to monoazo pigments of the

in which R1 denotes carbamoyl among other possible constituents; R² and R³ denote hydrogen or chlorine among other possible constituents; and A denotes phenyl among other constituents. The pigments generally have red shades and are eminently suitable for example for coloring lacquers, resins and printing inks.

The invention relates to dyes of the general formula (1)

in which

R1 denotes carbamoyl, carbamoyl bearing aryl as a sub- 60 stituent or amino bearing a C-acyl or a substituted Cacyl group as a substituent on the nitrogen atom;

R² denotes hydrogen, chlorine, bromine, alkoxy, cyano, carbomethoxy, methyl sulfonyl, carbamoyl or carbamoyl bearing aryl as a substituent;

R3 denotes hydrogen, chlorine, methyl or alkoxy,

R1 and R2 together may denote the radical of the formula:

2

A denotes phenyl, naphthyl, diphenyl, fluorenyl or anthraquinonyl which may bear chloro, cyano, alkyl, alkoxy or carboalkoxy as a substituent; and

B denotes a hydrogen atom or aryl of one to three rings which may be substituted and may contain ring hetero-

Alkoxy radicals for R2, R3 or A include for example methoxy and ethoxy. Alkyl and carboalkoxy radicals for A include for example methyl, ethyl, carbomethoxy and

Examples of radicals B (other than hydrogen) are methyl, phenyl, or phenyl, naphthyl or anthraquinonyl bearing, as substituents, chlorine, bromine, methyl, ethyl, methoxy, ethoxy, phenoxy, chlorophenoxy, phenyl, benzoyl, cyano, carbomethoxy, carbamoyl, sulfonamido, acetylamino, benzoylamino, chlorobenzoylamino, methylbenzoylamino or nitro, and also the radicals having the formula:

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Preferred radicals B include for example phenyl, or phenyl or naphthyl bearing, as substituents, chloro, methyl, ethyl, methoxy, ethoxy, phenyl, carbomethoxy, carbamoyl, sulfonamido, acetylamino, benzoylamino or methylbenzovlamino.

R² has the meanings given above. Examples of radicals R¹ are:

CONH2, CONHCONH2, CONHC6H4C, CONHC6H4Cl (0,m,p), CONHC6H4CH4CH4 (0,m,p), CONHC6H4OCH3 (0,m,p), CONHC6H4CH4CH2 (0,m,p), CONHC6H4Cl (2,4; 3,4; 2,5; 3,5)

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$$CONHC_{10}H_7$$
 (α,β), $CONH$

$$CONH-CONH-CONH-CONH$$
,

CONH—anthraquinonyl (α,β) , CONH—3—chloroanthraquinonyl- (β) , NHCO C_0H_5 , NHCO C_0H_4 Cl(o,m,p),

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20 and

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$$-NH-CO$$
 CO
 $N-CO$
 SO_2NH_2

Preferred radicals R¹ have the formula:

in which

R⁷ denotes hydrogen, fluoro, chloro, methyl, ethyl, methoxy, ethoxy, carbomethoxy, carbamoyl, sulfonamido, N-phenylsulfonamido or cyano;

R⁸ denotes hydrogen, chloro, methyl, methoxy or ethoxy; R⁹ denotes hydrogen, chloro, methyl or methoxy; and B has the above meanings.

N - phenylcarboxamide, N - chlorophenylcarboxamide, N-methylphenylcarboxamide, N-methoxyphenylcarboxamide and N-dichlorophenylcarboxamide are suitable as aryl-substituted carboxamides for R².

Dyes of the general formula (1a) are preferred:

in which

R⁴ denotes hydrogen, chloro, methyl, ethyl, methoxy ethoxy or phenyl;

75 R⁵ denotes hydrogen, chloro, cyano, methyl or methoxy;

R⁶ denotes hydrogen, chloro, methyl or methoxy; and R¹ and R⁵ together may denote the radical of the formula:

in which R¹ and B have the above meanings.

The radical of the said formula (R¹+R⁵) is preferably in the 3,4-position to the —CO—NH— group.

Another group of valuable pigments has the general formula (1b):

in which B, R⁴, R⁵ and R⁶ have the above meanings.
For the production of the compounds of formula (1), a diazo compound of an amine of formula (2):

(3)

may be reacted with a coupling component of formula (3):

An azo compound of formula (4)

in which Hal denotes bromine or, preferably, chlorine may be condensed with an amine of the general formula (5)

The compounds of formula (4) may be prepared by reaction of the diazo compound of an amine of formula (2) with β-hydroxynaphthoic acid followed by halogenation.

Examples of compounds of formula (2) are:

N-phenyl-3-aminophthalimide,

N-2'-chlorophenyl-3-aminophthalimide, N-3'-chlorophenyl-3-aminophthalimide, N-4'-chlorophenyl-3-aminophthalimide, N-2'-methylphenyl-3-aminophthalimide, N-3'-methylphenyl-3-aminophthalimide, N-4'-methylphenyl-3-aminophthalimide, N-2'-methoxyphenyl-3-aminophthalimide, N-3'-methoxyphenyl-3-aminophthalimide, N-4'-methoxyphenyl-3-aminophthalimide, N-2'-carbomethoxyphenyl-3-aminophthalimide, N-3'-carbomethoxyphenyl-3-aminophthalimide, N-4'-carbomethoxyphenyl-3-aminophthalimide, N-2',4'-dichlorophenyl-3-aminophthalimide, N-2',5'-dichlorophenyl-3-aminophthalimide, N-3',4'-dichlorophenyl-3-aminophthalimide, N-2',5'-dicarbomethoxyphenyl-3-aminophthalimide, N-2',4'-dimethylphenyl-3-aminophthalimide, N-2',5'-dimethylphenyl-3-aminophthalimide, N-3',4'-dimethylphenyl-3-aminophthalimide, N-3'-chloro-4'-methylphenyl-3-aminophthalimide, N-4'-chloro-3'-carbomethoxyphenyl-3-aminophthalimide. N-2'-chloro-4'-methoxyphenyl-3-aminophthalimide,

N-β-naphthyl-3-aminophthalimide,
45 N-(4'-phenyl)-phenyl-3-aminophthalimide,
N-3'-fluorenyl-3-aminophthalimide, or
N-β-anthraquinonyl-3-aminophthalimide.

The following are suitable amines of the formula (5):

3-benzoylaminoaniline, 4-benzoylaminoaniline, 3-chlorobenzoylaminoaniline. 4-chlorobenzoylaminoaniline, 3-dichlorobenzoylaminoaniline, 4-dichlorobenzoylaminoaniline, 3-chloromethoxybenzoylaminoaniline. 4-chloromethoxybenzoylaminoaniline, 3-methoxybenzoylaminoaniline, 4-methoxybenzoylaminoaniline, 3-methylbenzoylaminoaniline, 4-methylbenzoylaminoaniline, 3-α-naphthoylaminoaniline, 4-α-naphthoylaminoaniline, $3-\beta$ -naphthoylaminoaniline, $4-\beta$ -naphthoylaminoaniline, $3-\beta$ -anthraquinonocarbonylaminoaniline,

4-β-anthraquinonocarbonylaminoaniline,
3-trichlorobenzoylaminoaniline,
4-trichlorobenzoylaminoaniline,
3-methoxy-4-benzoylaminoaniline,
3-methoxy-4-β-naphthoylaminoaniline,
3-methyl-4-benzoylaminoaniline,
3-methyl-4-β-naphthoylaminoaniline,
3-methyl-4-β-naphthoylaminoaniline,

2-methoxy-4-benzoylaminoaniline, 2-methoxy-4-trichlorobenzoylaminoaniline, 2-methoxy-4- β -naphthoylaminoaniline, 2-methoxy-5-chloro-4-benzoylaminoaniline, 2-methoxy-5-chloro-4-β-naphthoylaminoaniline 2-methyl-4-benzoylaminoaniline, 2-methyl-4- β -naphthoylaminoaniline, 2-methyl-4-chloro-5-benzoylaminoaniline, 3-aminobenzoic acid chloroanilide, 4-aminobenzoic acid chloroanilide, 3-aminobenzanilide. 4-aminobenzanilide, 3-aminobenzodichloroanilide, 4-aminobenzodichloroanilide, 3-aminobenzo-β-naphthylamide, 4-aminobenzo-β-naphthylamide, 3-aminobenzoyl-α-aminoanthraquinone, 4-aminobenzoyl-α-aminoanthraquinone, 3-aminobenzotrichloroanilide, 4-aminobenzotrichloroanilide, 3'-aminobenzoyl-4-aminodiphenyl, 4'-aminobenzoyl-4-aminodiphenyl, N-phenyl-4-aminophthalimide, 4-aminophthalimide, N-(4'-chloro)-phenyl-4-aminophthalimide, N-(2'-chloro)-phenyl-4-aminophthalimide, N-(2',4'-dichloro)-phenyl-4-aminophthalimide, N-(2'-carboxymethyl)-phenyl-4-aminophthalimide, N-(4'-methoxy)-phenyl-4-aminophthalimide, N-phenyl-3-aminophthalimide, and 3-aminophthalimide.

Compounds of formula (4) are obtained by conventional methods from the appropriate carboxylic acid by reaction with halogenating agents such as POCl₃, SOCl₂ or COCl₂, preferably in an inert solvent such as nitrobenzene, a halobenzene or a xylene with the addition of a catalytic amount of dimethylformamide or pyridine.

Condensation of the azocarboxylic chlorides or bromides of formula (4) with the amines of formula (5) is advantageously carried out by heating in organic solvents such as o-dichlorobenzene, nitrobenzene, methyl benzoate, xylene, dimethylformamide or N-methylpyrrolidone, and acid-binding agents or a catalytic amount of a compound such as collidine or N-methylpyrrolidone may be added 45 which accelerate the reaction at temperatures of more than 100° C.

The coupling component of formula (3) may be prepared for example by condensation of 2-hydroxynaphthalene-3-carboxylic acid chloride with an amine of 50formula (5) or by condensation of 2-hydroxynaphthoic acid (3) with an amine of formula (5) in the presence of a chlorinating agent such as PCl₃.

Coupling of the compounds of formula (3) is advantageously carried out by bringing the aqueous alkaline solution of the coupling component or a very finely divided suspension of the coupling component in water together with the acid diazo solution. A pH range of from 4 to 7 is adjusted (advantageously by adding a buffer such as sodium acetate) and the addition of wetting or dispersing agents, for example aralkyl sulfonates, makes for a uniform course of the reaction. The new dyes may also be prepared by the modified process of French Pat. No. 1,537,423.

The pigments of the invention are obtained in this way in a very pure chemical condition but occasionally not in the optimum physical form for all applications. They may be brought into the form adapted to the particular application by conventional measures such as size reduction, salt grinding or recrystallization.

The new pigments may be used for dope dyeing for example of viscose, for the production of colored print pastes for book or offset printing, for the production of colored surface coatings, for example nitrocellulose lac- 75 prepared from the pigment obtained.

quers, acrylate lacquers, melamine resin lacquers or alkyd resins, for dyeing phenoplasts or aminoplasts or thermoplastics such as polystyrene, polyolefins or polyvinyl chloride, rubber or silicone resins, for dyeing laminate papers or boards and for textile printing.

The new pigments are particularly suitable for dyeing polyvinyl chloride, polyethylene or polypropylene and in coating compositions and high grade printing inks.

The following Examples illustrate the invention. Unless 10 otherwise stated the parts and percentages are by weight; the temperatures are given in degrees C.

EXAMPLE 1

288 parts of the dye obtained by coupling diazotized 15 N-phenyl-3-aminophthalimide with 2-hydroxynaphthoic acid-3 is heated with 2600 parts of o-dichlorobenzene, 260 parts of thionyl chloride and 8 parts of dimethylformamide at 110° to 120° while stirring for five hours.

After the reaction mixture has cooled, the uniformly crystalline azo dye monocarboxylic acid chloride is isolated by suction filtration, washed with 200 parts of o-dichlorobenzene, then with 1000 parts of benzene and then with 1000 parts of cyclohexane and dried at 80° at subatmospheric pressure. 266 parts of a red crystal powder is obtained.

-Calculated: Cl=7.8%. Found: Cl=7.6%. Analysis.-22.8 parts of the azo dye carboxylic acid chloride thus obtained is stirred into 800 parts of dry o-dichlorobenzene, then 12.7 parts of finely powdered 4-benzoylaminoaniline 30 and 5 parts of dimethylformamide are added and the whole is then heated for five hours at 140° to 150°. After cooling the whole to 80° the deposited sparingly soluble pigment is suction filtered and washed with a little hot o-dichlorobenzene and then with cold methanol until the filtrate running away is clear. The pigment can be improved by boiling it up with methanol or another solvent for two hours or stirring it at room temperature, preferably with N-methylpyrrolidone. After the product has been dried at 80° at subatmospheric pressure, 22.0 parts of a red powder is obtained which is practically insoluble in the usual solvents. Polyvinyl chloride film and sheeting and lacquers are colored red shades having excellent fastness to light, migration and overcoating.

The pigment has the formula:

Analysis.—Calculated: N=11.1%. Found: N=11.3%. Other monoazo pigments are obtained with the components in the following Table by coupling 1 mole of the diazo compound of the amine specified in column (I) onto 1 mole of 2-hydroxynaphthoic acid-(3), converting the resultant monoazo dye carboxylic acid into the acid chloride and condensing it with 1 mole of the amine specified in column (II).

Column (III) indicates the shade of a lacquer coating

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	mple:	Cı	Yellowish
٠.	$N-\langle 0 \rangle$	H ₂ N-\ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \	Yellowish red.
;	NH ₂ Same as above		Red
	, b	H ₁ N-O-O-O-CI	
•		H ₁ N-Cl	Red.
		δι Cl	n-4
•	5do	H ₂ N- C1	Red.
		CI CI	
1	3		Red.
	out only		
		H ₂ N-\ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \	
•	7	H ₃ N-\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\	Redi
		$\langle \overline{\circ} \rangle$	
	3do	H ₂ N- NHOC S O ₂ NH ₂	Red;
•),do,	H ₂ N-\ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \	Red:
,	do		Red.
•		H ₂ N-\ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \	2100
	11do		Browns
		H ₂ N-\ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \	
		Cı	•
1	2do	- осн,	Bluish red.
		H ₂ N-\O-\O-\O-\O-\O-\O-\O-\O-\O-\O-\O-\O-\O-	
1	8do	H ₂ N-\-\-\-\-\-\-\-\-\-\-\-\-\-\-\-\-\-\-\	Yellowish red.
,			
	4do	- Cl	Dos
•	ar and a second and a second are a second as a second are a second as a second are a second as a second are a	H ₂ N-NHOC-	
		· · · · · · · · · · · · · · · · · · ·	Dos
1	.5,,do,	H ₁ N - NHOC - CI	1506
	· ·		•
1	.6do	H ₂ N-NHOC-C1	Dos

I	II	IH. 1917
Example:		
17CO	CI l	Yellowish red.
\bigcirc \sim \sim	H ₂ N-NH0C-	
	<u>C1</u>	*
NH ₃		Red.
· · · · · · · · · · · · · · · · · · ·		2004.
	H ₂ N—NHOC—N	
	$\langle \rangle$	
19do	······································	
	H ₂ N NHOC S O ₂ NH ₂	Red.
		• •,
20dodo	·····	Red.
	H ₂ N-NHOC-	
	$\langle \circ \rangle$	
21dot_		Red.
<i>41</i>	H ₃ N-NHOC-	
	-CH ₃	
00	*	Bluish red.
22do	H ₂ N—NH0C—	Dittisti led.
	осн,	
23doto		Yellowish
	H ₂ N-COHN-COHN-COHN-COHN-COHN-COHN-COHN-COH	red.
24dodo	H ₂ N-COHN-COHN-	Do.
	CI	
25doarea_area_area_area_area_area_area_	H.N. COHN C	Do.
	H ₂ N—C0HN—C1	
26dotu-itu-itu-itu-itu-itu-itu-itu-itu-itu-i	H ₄ N-COHN-Cl	Orange red.
4	<u>cı</u>	
27do		Red.
	H ₂ N-COHN-Cl	
•	GI	and the second second second
28dodo		Bluish red.
	H ₂ N-COHN-COHN-	red.
	G1	11. 1
29do		Red:
	H ₂ N-C0HN-C1	
	င်၊	
30do	H ₂ N-COHN-CH ₈	
31dodo		Red.
	H ₂ N-COHN-COHN-CO	
• 1	<u>сн</u>	
32dodo	H ₂ N-COHN-COHN-	Yellowish red.
	CI	

The second secon	п		an fra treesant	The second second	eneros do nomena está como está de como está d	· · · · · · · · · · · · · · · · · · ·
Example: 33 Same as Example 2			<u></u>		1-277	Red.
bame as example 2	H ₂ N-	O >-coh	4 - 〈 () }	CH ₃		A. C.
·						
24			CH ₁			Dad
34dodo	H ₁ N-	Сони	√ (() >	-CH ₃		Red.
or de	,		Cl			37-31
35do	H ₂ N-<	О >-сони	~(O)	-C1		Yellowish red.
			СН			
36 0 do			CHI			n
36dodo	H ₂ N	—сони	~(O)			Red.
in the second of			OCH,			4 -
			COM			Red.
37do	H ₂ N-	О У∸сони	\prec \bigcirc \gt	-OCH		reu.
38do						Yellowish
90	H ₁ N-	○ >-сони	\prec \bigcirc \gt	-OCH:		red.
· ·· · · · · · · · · · · · · · · · · ·	. `		Cı			
39do			Cl			Red.
V/	······	_	آنے ر			2004.
·	H:N-<	O >-cohn	$\langle O \rangle$			
			осн			
40do			OCH,	H.		Red.
	······		ر الم			Neg.
	H ₂ N-	O >-cohn	\prec \bigcirc \gt			
			OCH:			
41do			()			Yellowish
The second secon	H ₂ N-<	○ ≻-сони	$\langle O \rangle$			red.
	_		CN			
42dodo						Do. .
	H ₂ N-(O >-cohn	\prec \bigcirc \gt	-C1 · · · · ·		20.
	`		CN			
43do	_	\overline{a}				Do.
_* vij	H ₂ N-(O >-cohn	$\prec \bigcirc \gt$	$\langle O \rangle$		
44do		$\overline{\sim}$				Do.
	H ₂ N-(COHN	$\times \bigcirc >$			
		. —	$\langle 0 \rangle$			
entinerio (f. 1905) Santa Santa (f. 1905)						
45do	H ₂ N-	COHN	_			D 0.
	133,4			-0-\		
46do			~ · · · · · · · · · · · · · · · · · · ·			Red.
				. ^		
	<u> </u>			()		
	H ₂ N-	-со-н				
	\sim	<u> </u>	\sim			
• •	*		0.		*********	e e e e e e e e e e e e e e e e e e e
47do			14.1 0			Yellowish red.
	The second of th	ĆĮĆI	_/\/\	\wedge		reu.
	· · · · · · · · · · · · · · · · · · ·	<u> </u>		\bigcirc		
	H ₂ N(○ >-сони	人人人	<u> </u>	· · · · · · · · · · · · · · · · · · ·	www. · · · · · · · · · · · · · · · · · ·
			ď	•		
48do		$\overline{}$:			Do.
. To all	H.N-(O >-cohn	CONH2		*.	D0,
49dodo						Do.
	H.N(O >-conh	$\langle \cup \rangle$	-SO:NH:		170.
	_					

I	II		III
Example: 50 Same as Example 2		он	Yellowish red.
	H ₁ N-	-сони	
. :		CH ₄	
51dodo	***************************************		Red.
e.com	H ₂ N-	-COHN-O	
52do			Yellowish
	H_3N-	-cohn-(O)-G-(O)	red.
53do	H ₂ N-	-COHN-\O_\-NHSO;-\O_\	Red.
54dodo	H ₂ N-()-	-conh-Conh-Conh	Yellowish red.
55do			Red.
	H ₂ N-	-COHN-CONH,	ř
56do	***************************************	CH ₁	Red.
	H ₂ N-	-COHN-O	
		Y Y	er en
57do	H ₂ N-\	-COHN-OCH	Red.
		СН	
58do	H ₂ N—COH		Yellowish red.
59do	н, N—Сон	IN—CI	Bluish red.
		Cl	
60do			Red:
	н, м—Сон		
		осн.	Yellowish
61 do 	H,N—COH	IN-CO-OCH:	red.
· · · · · · · · · · · · · · · · · · ·			
62do	^	C1	Do:
	H ₁ N—COH	N-()	
		Č I	
63do63		CI	Do.
	нисон		sansa kandi
		CH ₀	~
64dodo	H ₁ N-COH		Do.
	7	and the second second	
65do	H _i N-COH	IN-SO ₂ NH ₂	Red.
•		- 1 / 2	ere a la seguire de la companya de l
	•		

	TABLE—Continued	
I	II	III
Example: 66 Same as Example 2		70.1
oo Same as Example 2	H ₂ N-COHN-COH ₃	Red.
	CI	
<u>.</u>		
67do	H ₂ N—COHN—Cl	Yellowish red.
	\bigcirc	
	V ON	
68do		Red.
	H ₂ N—COHN	
	H ₂ N COHN	
69do		Red.
	H ₂ N—COHN—	
	\bigcirc \bigcirc	
70do	ÇН ₈	Yellowish
		Yellowish red.
	H ₂ N-CONH-CONH-CO	
	осн.	
71dodo	H ₂ N—CONH—CO	Red.
	-cı čı	
72dodo	H ₂ N—CONH—CONH	Reds
	-CH ₂ Ċ1	
73do	H ₂ N-COHN-COHN-	Red:
	OCH,	
74doto		Red.
75do		Orange.
	\wedge $ \bigcirc \rightarrow \langle \bigcirc \rightarrow \langle \bigcirc \rangle$	
	H ₂ N NHOC	
	V	
76dodo	C0 C0	Red.
	NHOO NHOO	
	H ₂ N————————————————————————————————————	•
77do	<u></u> Çı	Yellowish
	NH ₂ —CONH—CI	red.
	Cl	
78dodo	OCH;	Red.
	H ₂ N-CONH-CONH-	
	OCH ₂	
79do	NH2	Yellowish red.
	CONH-	

I	TABLE—Continued	III
Example 80 Same as Example 2		Yellowish red.
	H ₂ N-CO	
81dobdo	CO N-()-S O ₂ NH ₂	Red.
00	H ₂ N—CO	Bluish
82doturisia.e.e.	H ₂ N-NH	red.
83do	✓ `có ,co	Do.
	H ₂ N-CON-CON-CO	
84do	CO CO	Yellowish red.
	H_2N	
85 <u></u> do <u></u>	N-()-C1	Red.
86do	H ₂ N — CO	Bluish red.
•	H_2N — $C1$	reu.
87 <u></u> -do ₌₌₌		Red:
	H ₂ N CO COOCH ₅	
88 .do	N-()-0CH ₁	Bluish red.
	H ₂ N-C0	Red:
89do	H ₂ N-CO OCH ₄	
90dodo	CO N-	Yellowisi red.
	H ₂ N CO CH ₄	
91dodo	H ₂ N-CON-CO	Yellowisi red.
92 .do	C0	Yellowis red.
	H ₂ N CO Cl	

I	II	III
cample: 93Same as Example 2	^ C0	Red.
39bame as Example 2	N—————————————————————————————————————	Red.
	$_{\mathrm{H_2N}}$	•
94do	Co	Yellowi red.
	H_2N —C1	
	CO CN	
95do	CO N-CONH ₂	Red.
	H_2N	
96do		Orange red.
	$\bigcirc \bigcirc \qquad \qquad \bigcirc \bigcirc$	
	NH ₂	
97dodo	^ CO	Orange.
	N—CONH—CO	
	ŃH₂	
08dodo		Yellow red.
	H ₂ N — CH ₃	
)9do		Bluish
	$N-\langle O \rangle$	red.
	H_2N CO C_1	
100	H ₂ N-CONHCONH ₂	Yellowi red.
$\bigcirc \qquad \searrow \qquad \bigcirc \searrow$		
NH ₂		
01 Same as above	C1	Red.
	H ₂ N-\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\	
	E ₁	
102dodo	Co	Yellowi red.
	H_2N N	
	V '00	Dhutah
103doi	C0	Bluish red.
	$_{ m H_2N-}$	
104		Yellowi red.
N-()-cı	H₂N-CONHCONH₂	red.
ŃH₂		

	TABLE—Continued	
I	II	III
xample: 105 Same as Example 104		Red.
106do	H ₂ N-OC-O	Reddish brown
107do	H ₂ N-CONH-SO ₂ NH ₂	Yellowing red.
108do	H ₂ N-CON-CO	Brownis red.
109do	$\begin{array}{c} CO \\ N \end{array}$	Red.
110do	CO NH	Redz
111		Red:
NH ₂ CO N COOCH ₃	H ₂ N-CONHCONH ₂	Yellow red.
113 Same as above	-SO2NH2	Ređi
114dodo	H ₂ N-NHOC-	Red:
115dodo	C1 H ₂ N-\NH0C-\	Red:
116dodo	-NHOC-	Yellow red;
117dodo	H ₂ N-CO NH	Reda
118dodo		Yellow red.

30

35

34.2 parts of the azo dye carboxylic acid chloride obtained according to Example 1 is stirred in 600 parts of N-methylpyrrolidone-(2), then 23.8 parts of finely powdered N-phenyl-4-aminophthalimide is added and the whole is heated for five hours at 140° to 150°. The sparingly soluble pigment thus precipitated in finely crystalline form is cooled to 80° and suction filtered, and washed with N-methylpyrrolidone-(2) and then with cold methanol until the filtrate running away is clear. The pigment can be improved by boiling it up for two hours in methanol or another solvent or stirring it at room temperature.

After drying at 80° at subatmospheric pressure 45.0 parts of a red powder is obtained which is practically insoluble in the usual solvents. Polyvinyl chloride film, sheeting and coating compositions are colored therewith red shades having excellent fastness to light, migration and overcoating.

The pigment has the formula:

Analysis.—Calculated: N=10.7%. Found: N=10.6%. Other monoazo pigments are obtained with the components in the following Table by coupling 1 mole of the 40 diazo compound of the amines specified in column I with 1 mole of 2-hydroxynaphthoic acid-(3), converting the resultant monoazo dye carboxylic acid into its acid chloride and condensing this with 1 mole of the amine specified in column II.

Column III indicates the shade of a coating prepared with the pigment obtained.

cording to Example 1 is heated to about 80° in 1600 parts of dry o-dichlorobenzene. Then a hot solution of 29.6 parts of 3 - chloro - 4 - benzoylaminoaniline in 200 parts of N - methylpyrrolidone-(2) or dimethylformamide is added and the whole is heated for five hours at 140° to 150°.

The sparingly soluble pigment thus deposited in a finely crystalline form is cooled to 80°, suction filtered, and washed with a little o-dichlorobenzene or cold dimethylformamide or N - methylpyrrolidone-(2) and then with cold methanol until the filtrate running away is clear. The pigment may be improved by boiling it up with methanol or another solvent for another two hours or stirring it at room temperature.

After drying at 80° at subatmospheric pressure, 56.0 parts of a red powder is obtained which is practically insoluble in the usual solvents. Polyvinyl chloride film, sheeting and coating compositions are colored therewith red shades of excellent fastness to light, migration and overcoating.

The pigment has the formula:

Analysis.—Calculated: N=10.5%. Found: N=10.7%. Other monazo dyes are obtained with the components in the following Table by coupling 1 mole of the diazo compound of an amine specified in column I with 1 mole of hydroxynaphthoic acid-(3) and converting the monoazo dye carboxylic acid obtained into its acid chloride which is then condensed with 1 mole of an amine specified in column II.

I	п	III
Example number: 120CO	- Han- NHCO	Cl Red.
NH ₂ 121 Same as above	H ₂ N——NHOC	Red:
122do	H ₂ N-OCH ₅	Bluish red;
123do	Н2N-С1	Red:

	TT	III
Ex. I 125 CO	п	Red.
N-CO	H ₂ N-\ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \	
NH2		m
126 Same as above	H ₂ N-OCH ₃	Bluish red.
127do		Red.
	H ₂ N — NH O C — N	
128do		Red:
	H ₂ N-\ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \	
129do	H_2N- COHN $-$ Cl	Orange
130do	H_2N —COHN—	Red.
131= CO	H ₂ N————————————————————————————————————	Red.
132 CO NH ₃	Same as above	Red:
133 CO N CO N CO	H ₂ N-\-\-\-\-\-\-\-\-\-\-\-\-\-\-\-\-\-\-\	Red.
134_a== CO N- CO NH ₃	Same as above	Red.
135 CO NH ₃	do	Red.

Ex. I	П	III
136 NH ₂	H_2N —NHOC—C0 CO CO CI CO CI	Bluish red.
137 Same as above	H ₂ N — NHO C — C1	Brown- ish red.
138do	H_2N —NHOC— CO N — CO OCH_3	Red.
139do	H ₂ N—NHOC—CO	Orange.
140do	H ₂ N-_NH0 C-_C0	Red.
141do	H ₂ N—OCON—OCO	Red.
142do	H ₂ N-NHOC-CO	Brown ish rd. e-
143do	H_2N N CO CO CO CO CO CO CO CO	Bluish red.
144do	H_2N $NHOC$ CO $COOCH_3$	Brownish red.
145d0	H ₂ N—NH0C—NH0C	Red.

Ex. I	П	III
146NH ₂	H_2N —NHOC— CO N — CI OCH_3	Red.
147 Same as above	H_{2N} N OCH_{4}	Red.
148do	H_2N —NHOC— CO CH_3	Red.
149do	H_2N $NHOC$ CO OCH_3	Red.
150do	H_2N —NHOC— CO CO CH_3	Yellowish red.
151do	H ₂ N-CON-CH ₄	Do.
152do	H_2N —NHOC— CO N —CH ₃	Do.
153do	H_2N —NHOC— C_0 C_1	Do.
154do	H_3N —NHOC— CO CI CI CO OCH_3	Do. Red.
155do	H ₂ N-OC-OC1	
156do	$\begin{array}{c c} & & & & & & & & & & & & & & & & & & &$	Yellow- ish red.
157do	H ₂ N-OC-ONH ₂	Red:

Ex. 1	II	III
158Same as Example 136	^CO	Red.
	H ₂ N-O-SO ₂ NH ₂	·
159do	- ^co	Red.
	H ₂ N	
160do	- ^00	Red.
	H ₂ N-O-NHOC-O-O-O-O-O-O-O-O-O-O-O-O-O-O-O-O-O-O-	
161do	- ^co	Red:
	H ₂ N—NHOC	
162do	co co	Yellow- ish red.
	H ₂ N-OC-OCON-CO	red.
163 do	C0 C	Red.
	H ₂ N—NH0C—CO	
164do		Reds
	H ₂ N——NHOC—CO	
165do		Yellow-
	H ₂ N-NHOC-CO	Yellow- ish red.
166do	, co	Do.
	H ₂ N-O-NHOC-CI	
167do	CO OCH,	Red:
	H ₂ N-NHOC-OCH ₃	
168do		Yellow- ish red.
	H ₂ N-COOCH ₄	404.

Ex. I	II	III
169Same as Example 136	Co	Red.
	H ₂ N—NHOC	
	Со осн.	
	, CO	Vallow-
170dot		Yellow- ish red.
	H ₂ N—NHOC	
171do	CO OCH ₃	Orange:
	\sim N- \sim	
	H ₂ N—NHOC—CO	
•		
172do 	_\c^c_0	Yellow- ish red.
	N-O-O	red.
·	H ₂ N-OC-CO	
173doto	Co	Red.
	H ₂ N-\ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \	
	~ °c6	Red:
174do	Çı Çı	1.04
	H ₂ N————————————————————————————————————	
175do 	\ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \	Violet:
	\sim \sim \sim	
	H ₂ N-OC-COOCH ₃	•
	-осн	
176do	\ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \	Red.
e		
	H ₂ N—NHOC	
	V 60 0	
	<u> </u>	Red.
177 CO	H ₂ N-CONH-CONH-CONH-CONH-CONH-CONH-CONH-CON	1100.
N-CH3		
NH ₂		
178 CO	^ co	Yellow- ish red.
$N-\langle O \rangle$	$N-\langle O \rangle$	red.
CO CH ₈	H ₂ N-C0	
ŃH₂		_
179	H ₃ N-CONH-C1	Red.
N	C1	
CO NH ₃		
NH ₃		

Ex. No. I III

180....
$$CO$$

$$NH_2$$

$$NH_2$$

$$NH_3$$

$$NH_4$$

$$NH_2$$

$$NH_3$$

$$NH_4$$

$$NH_4$$

$$NH_4$$

$$NH_5$$

$$NH_6$$

$$NH_6$$

$$NH_6$$

$$NH_6$$

$$NH_7$$

$$NH_8$$

$$NH_8$$

$$NH_8$$

$$NH_8$$

$$NH_8$$

$$NH_9$$

EXAMPLE 182

288 parts of the dye obtained by coupling diazotized N-phenyl-3-aminophthalimide with 2-hydroxynaphthoic 20 acid-(3) is heated for five hours at 110° to 120° with 2600 parts of o-dichlorobenzene, 260 parts of thionyl chloride and 8 parts of dimethylformamide while stirring.

After the reaction mixture has been cooled, the uniformly crystalline azo dye monocarboxylic acid chloride 25 is isolated by suction filtration and washed with 200 parts of o-dichlorobenzene, then with 1000 parts of benzene and then with 1000 parts of cyclohexane.

After drying at 80° in vacuo, 266 parts of a red crys-

tal powder is obtained.

Analysis.—Calculated: Cl=7.8%. Found: Cl=7.6%. 22.8 parts of the azo dye carboxylic acid chloride thus obtained is stirred in 500 parts of N-methylpyrrolidone-(2); then 28.5 parts of the finely powdered amine having the formula:

is added and the whole is heated for five hours at 140° to 150°. The sparingly soluble pigment which is thus deposited in finely crystalline form is cooled to 80°, suction filtered and washed with N-methylpyrrolidone-(2) and then with cold methanol until the filtrate which runs away is clear. The pigment can be improved by boiling it up for two hours with methanol or another 50 solvent or stirring it at room temperature.

After drying at 80° in vacuo, 29 parts of an orange red powder is obtained which is practically insoluble in the usual solvents. Polyvinyl chloride film, sheeting and surface coatings are colored orange red shades having very good fastness to light, migration and overcoating.

The pigment has the formula:

Analysis.—Calculated: N=10.95%. Found: N=11.0%.

Other pigments are obtained with the components in the following Table by coupling the diazo compound of an amine specified in column I, with 2-hydroxynaphthoic acid-(3) and converting the monoazo dye carboxylic acid obtained into its acid chloride which is then condensed with an amine specified in column II.

Column III indicates the shade of coatings prepared with the pigment obtained.

Ex. No. I	п	
183 CO N-	H ₂ N—NH0C—CO	Red.
184 Same as above	H ₂ N——NH0 C——NH	Bluish red:
185do	H ₂ N————————————————————————————————————	Redi

Ex. No. I	п	m
186 Same as Example 183	C1 NHOC	Red.
187do	CO CI OCH ₈	Chestnut.
188do	H_2N $NHOC$ CO Cl H_2N OCH_8	Do.
189do	H ₂ N-NHOC-NHOC-	Red.
190do		Red.
191do		Yellowish red.
192do	H ₂ N-NHOC-CONCH _a	Red.
193do	H ₂ N——NHOC—CO	Chestnut.
194do	H ₂ N-NHOC-NHOC-C1	Red.
195do	H ₂ N — NHOC — CO CH ₃	Orange.
196doarea area area area area area area a	H ₂ N-NHOC-NHOC	Red:
197do	H_2N H_3O N CO CI CO CI CO CI	Red.

4	
4	

Ex. No. I	ш	ш
198 Same as Example 183	H ₂ N-————————————————————————————————————	Red.
199do	go gr	Red.
200do	H ₂ N-NHOC-CH ₂	Red.
201do	H ₂ N NHOC CO CO CO	Red.
202do	H ₂ N — NHO C — C1	Red.
203dot=============================	H ₃ N — NHOC — COOCH ₃	Yellowish
204do	H ₂ N NHOC CO COOCH ₄	Do.
205do	H ₂ N NHOC CO N OCH ₂	Orange.
208dot	H ₄ N————————————————————————————————————	Brown.
207do	H ₄ N—NH0C—CO	Red:

$\begin{array}{cccccccccccccccccccccccccccccccccccc$	Ex. No. I	n	m
210	208 Same as Example 183	OCH ₃	Brown.
210	209do	H ₂ N—NHOC	Red.
211do	210do	H ₂ N——NHCO—N——N	Red.
212do	211do	H ₂ N——NHOC—NHOC—NOCH ₃	Red.
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	212do		Bluish red
214. do	213do	H ₃ N—NHOC	Red.
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	214do	C1 NHOC	Red.
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	215do	H ₃ N—OCH ₃	Red.
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	216:do	H ₂ N-NHOC-NHOC	Chestnut.
218do		H ₂ N-NHOC-NHOC	Red.
219do		H ₂ N-NHOC-NHOC	Brown.
, CO	219do	Cl N-OCH ₈	Red:

Ex. No. I		П	III	
220 Same as E	xample 183	H ₂ N-NHOC-CON-CO	Red.	l•
221do		H ₂ N-NHOC-CO	Red.	
222do		н ₂ N—С	Red.	.•
223do		H ₂ NNHOC	Red.	• •
224do		-NHOC-CO Br	Red.	•
225do		H ₂ N-NHOC-CO	Red.	.•
226do		H ₂ N-NH0C-CON-C	Red.	•
227do		C1 -NH0C- C0 C	C1 Red.	•
228do		H ₂ N-NHOC-CON-C	Cl Red.	•
229do		H ₂ N-NHOC-CO CO OCH ₃	H₃ Oran >—Cl	ıge.
230do	,	H ₂ N-NH0C-CO	CH ₂ Red.	•
231do		H ₂ N-NH ₀ C-N	Cl Red.	Seg

Ex. No. I	п	m
232 Same as Example 183	H ₂ N—NHOC—NHOC—	Red.
233do	CO CH ₃ CH ₃ CO CH ₃ CH ₃	Orange.
234do	N ₂ H——NHOC—NO	Red:
235do		Red:
236do	H_2N $NHOC$ CO CH_3 CO CH_3	Yellowish red.
237do	H ₂ N-CH ₃	Reda
238do	H ₂ N — NH0C — CO OC OC	Yellow.
239do	H ₃ N—NHOC—CO	Orange.
240do	$\begin{array}{c} \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ $	Reds
241do	H_2N —NHOC— CO CH_3 OC_2H_4	Reds
242do	H_2N $NHOC$ CO CH_8 OC_2H_5	Reds

Ex. No. I	п				m 1937.
243 Same as Example 183			vco		Red.
	H ₂ N	NHOC-	N		
			`co'		
244do	·····		,co	осн³	Red.
	· · · · · · · · · · · · · · · · · · ·		N-C	осн.	
."dy	H ₂ N	NHOC-	/\co		
245do			00	OC2Hs	Red.
	H ₂ N	NHOC-) N-(
,	****		CO 002	H ₆	
246do			©0.	•	Reda
			N-		
	H ₂ N	у————————————————————————————————————	\\\co	C ₂ H ₅	
247do			CO	СН.	Red:
	H ₂ N	NHOC-	Co	·CH ₄	
248do			00	CH,	Brown reds
	H₂N		N-		***************************************
	11213	- Milou-	\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\	Ċн,	
249do	<u></u>		Co Co	_C₂H₅	Red.
. "	H₂N		Co/N-		
250do	••••••		,co	_	Yellowish red.
•	H₂N	NHOC_	N-K	C_2H_{δ}	
1.		V.	` CO	en e	की है। कार का का का का की की है।
251do		News #	,co	ÇH ₁	Red.
			N-		Ivod.
	H ₂ N	NHOC	co	сн ,	
200 do				CH.	The de
252do		CI	N-	CH ₂	Reda
# A	H ₂ N	-VHOC-			a exercised to
253do			Co	CH,	Reda
	H₂N		CONT	сн,	
			~~		

Ex. No.	ī	п	m
254	Same as Example 183	C0 C1	Red.
	W	H ₂ N-NHOC-CO OCOCH ₃	
•		00 000011	
255	do	co .	Red.
		H ₂ N-NHOC-NHOC-N-OCOCH ₂	
256	dodo	C0 C1	Red.
		H ₂ N-NHOC-NHOC-N-OSO ₂ -	
		√ °C6 d₁	
257	dodododo	C1 CO	Red.
		H ₂ N—NHOC—CO OCOCH ₂	
258		- CO	Red.
	δ_{μ}	H ₂ N-NHOC-N-OCOCH ₃	
259=	do	· 'co	Red.
		N———SO ₂ CH ₃	
		H ₂ N-NHOC-CO CI	
260	do	. Co	Red.
		H ₂ N-NHOC-CO SO ₂ CH ₂	
	A graph		
261,	ado	- 000 —	Red.
		H ₂ N-NHOC-NHOC-CH ₃	
		со волсня	
262	do	C1	Red.
		H ₂ N-NHOC-Cl	
263	a.ms. do 	, Co	Chestnut.
		H ₂ N Co C ₁	
264	do	H ₂ N-COHN-CH ₂	Yellowish red.
265	đo	H ₁ N-COHN-	Red.
267	do	H ₂ N—COHN—COHN—	Yellowish red.
			AUU.

Ex. No. I	п		ш
268 Same as Example 183	H ₂ N—COHN—OCH ₃		Red.
269do	E COHN—COHN—COHN—COHN—COHN—COHN—COHN—COHN—	and the second second	Orange.
	Cl		*****
270do	H ₂ N—COHN—Cl		Red.
271 CO NH ₃	H ₂ NNHOCN		Red.
272 Same as above	H ₁ N—NHOC		Red.
273do	C1 C1 C1 C1		Red.
274do	H ₂ N-NH0C-CON-OCH ₃		Red.
275do	H ₂ N-CONH-C1		Yellowish red.
276 CO N-CH ₃	$\begin{array}{c c} & & & & & & & & & & & & & & & & & & &$		
277 Same as above	H ₂ N-CO Cl		Bluish red.
278do			Red.
279do	C1 NHOC-C1		Red.
280do	H_2N —COHN—C1		Orange:
281OON_OCH	H ₂ N-NHOC-CO CI	>	Reda

Ex. No. I	п	пі
282 Same as Example 281	$_{ m H_2N}$ —COHN—	Red.
283do	H ₂ N—Cl Cl Cl	Bluish red.
284do	H ₂ N——NHOC——C1	Red.
	3.757.77.4	

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45

or

EXAMPLE 1

Use in coating compositions

5 parts of the dye obtained according to Example 119 and 95 parts of a baking lacquer mixture (for example 70% of coconut alkyd resin, 60% in xylene, and 30% of melamine resin, about 55% in a mixture of butanol and xylene) are ground in an attrition mill. After application to a substrate and baking for thirty minutes at 120° brilliant full shade coatings are obtained with very good fastness to light and overcoating.

Brilliant white brightening effects are achieved by adding, for example, TiO₂.

Similar coatings in the specified shades are obtained by using the pigments described in the other Examples.

EXAMPLE 2

Use in plastics

Transparent colorations of polystyrene having very good fastness to light are obtained by incorporating 0.05 part of the dye obtained according to Example 1 in 100 parts of polystyrene. Coloration is carried out at 190° to 220° in an extruder.

Polystyrene colorations having good hiding power are obtained analogously by incorporating 0.2 part of the abovementioned dye and 1.0 part of TiO₂ into 100 parts of polystyrene.

Similar results are obtained when the pigments from the other Examples are used.

EXAMPLE 3

Use in printing inks

5 parts of the dye obtained according to Example 26, 30 to 40 parts of resin (for example rosin modified with phenol-formaldehyde) and 65 to 55 parts of toluene are intimately mixed in a dispersing unit. A toluene intaglio printing ink having excellent light fastness and outstanding brilliance is obtained.

When the pigments from the other Examples are used, printing inks having similar properties and the specified shades are obtained.

We claim:

1. An azo pigment of the formula:

in which R¹ is

NHCO-N-B

R² is hydrogen, chloro, bromo, methyl, methoxy, ethoxy, cyano, carbomethoxy, methylsulfonyl, carbamoyl, N - phenylcarbamoyl, N - chlorophenylcarbamoyl, N-methylphenylcarbamoyl, N-methoxyphenylcarbamoyl, N-dichlorophenylcarbamoyl;

R³ is hydrogen, chloro, methyl, methoxy or ethoxy;
R¹ is hydrogen, fluoro, chloro, methyl, ethyl, methoxy, ethoxy, carbomethoxy, carbamoyl, sulfamoyl, N-phenyl-sulfamoyl or cyano;

R8 is hydrogen, chloro, methyl, methoxy or ethoxy;

R⁹ is hydrogen, chloro, methyl or methoxy;
A is phenyl, or phenyl substituted by chloro, cyano, methyl, ethyl, methoxy, ethoxy, carbomethoxy or carboethoxy, naphthyl; or diphenyl; and

B is hydrogen; methyl, phenyl or phenyl substituted by chloro, bromo, methyl, ethyl, methoxy, ethoxy, phenoxy, chlorophenoxy, phenyl, benzoyl, cyano, carbomethoxy, carbamoyl, sulfamoyl, acetylamino, benzoylamino, chlorobenzoylamino, methylbenzoylamino or nitro; naphthyl; chloronaphthyl; or one of the radicals having the formula

CH₃

2. A dye as claimed in claim 1 of the formula:

in which

R4 denotes hydrogen, chloro, methyl, ethyl, methoxy, ethoxy or phenyl;

R⁵ denotes hydrogen, chloro, cyano, methyl or methoxy; R⁶ denotes hydrogen, chloro, methyl or methoxy; and R¹ and R⁵ together may denote the radical of the formula

R¹ and B having the meanings given in claim 1.

3. A dye as claimed in claim 1 of the formula:

in which B, R^4 , R^5 and R^6 are meanings given in claim 1.

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FLOYD D. HIGEL, Primary Examiner

U.S. Cl. X.R.

8—4; 106—23, 288 Q, 300, 308 Q; 117—138.8 UA; 35 260—41 B, 41 C, 154, 155, 156, 326 D, 326 N

UNITED STATES PATENT AND TRADEMARK OFFICE CERTIFICATE OF CORRECTION

PATENT NO. :

3,825,527

DATED

July 23, 1974

INVENTOR(S): GUENTHER RUIDER and PETER DIMROTH

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 1, in the heading, insert--Claims

Priority, Application German, December 4, 1970, P 20 59 708.4--

Column 2, line 61, delete "CONH $_6$ C $_4$ Br" and

substitute--CONHC6H4Br--;

Column 3, line 25, delete "NHCO

and substitute--NHCO

Column 10, line 25, delete "H2N

and substitute--H2N NHOC

Column 17, Example 78, delete "CONH" and substitute--COHN--;

UNITED STATES PATENT AND TRADEMARK OFFICE CERTIFICATE OF CORRECTION

PATENT NO. :

3,825,527

Page 2

DATED

July 23, 1974

INVENTOR(S):

GUENTHER RUIDER and PETER DIMROTH

It is certified that error appears in the above—identified patent and that said Letters Patent are hereby corrected as shown below:

and substitute-- NH--;

Column 37, Example 180, delete "OCH $_3$ ", at the end of the formula;

Column 40, Example 186, delete " H_2N NHOC" and substitute- H_2N NHOC--;

Column 42, Example 203, delete "Yellowish" and substitute--Yellowish Red--;

Column 42, Example 204, delete "Do." and substitute--Yellowish Red--;

Column 54, Example 271, second formula, delete Cl " ${\rm H_2N}$ " And substitute-- ${\rm H_2N}$ NHOC--;

Column 54, Example 276, far right side insert

Signed and Sealed this
twentieth Day of January 1976

[SEAL]

Attest:

RUTH C. MASON
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents and Trademarks